AUTOCLAVE SECONDARY WASTE
VX ON DPE AND WOOD

Interim Report

Prime Contract DACA87-89-C-0076
Subcontract G51972
SwRI® Project 01.14121

Prepared by:

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October 3, 2008

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1. INTRODUCTION

The Tooele Chemical Agent Disposal Facility (TOCDF) is currently planning for processing of secondary and closure wastes. Installation of a system specifically for processing of secondary wastes would allow parallel processing of secondary wastes, increase the availability of the Metal Parts Furnace (MPF) to process munitions, and shorten the facility's overall schedule. In an earlier study, Continental Research & Engineering (CR&E) conducted an investigation of processing alternatives and found that the treatment of secondary waste through an autoclave is an attractive processing alternative due to its relative low cost and short implementation schedule. In addition, autoclaves have been used successfully by the Army for decontamination of BDO suits contaminated with chemical agents GB and VX, and Battelle has evaluated HD destruction in an autoclave environment for the Pueblo Chemical Agent-Destruction Pilot Plant Project (PCAPP).

In this project, Southwest Research Institute® (SwRI®) was tasked to conduct decontamination experiments using a commercial-off-the-shelf (COTS) bench model autoclave. The objectives of the test program were to: (1) obtain analytical results documenting the capability of an autoclave system to decontaminate secondary wastes contaminated with chemical agents (i.e., 'proof-of-concept' tests); and (2) document the operating/processing parameters (temperature, time, pressure, and vacuum) needed by the bench model autoclave to achieve a given level of decontamination performance.

To date, SwRI® has completed autoclave tests to treat DPE and wood contaminated with neat VX agent. Those results are summarized in this interim report. Testing of charcoal contaminated with VX, and all three waste matrices contaminated with chemical agents GB and HD, is continuing and will be reported in a final report.

2. EXPERIMENTAL APPROACH

2.1 Test Procedure

The experimental approach for the test program is detailed in "Test Plan for Barnstead – Harvey Autoclave Agent Testing," Draft – E, Revision 2, dated July 7, 2008. The Test Plan presents a detailed description of the operational and test procedures employed during the experiments, and it is referenced here for additional information.

A couple of modifications to the original test plan had to be adopted as the capabilities of the autoclave became apparent and impediments to the original vapor monitoring technique were discovered during early tests. These are discussed in Section 3.1. The modifications were necessary to yield reproducible test results indicative of the autoclave performance. A synopsis of the current testing procedure follows:

- A 10-gram sample of the secondary waste matrix (DPE, wood, or charcoal) is spiked with 900 micrograms (µg) of neat chemical agent.

- The spiked sample is placed on a tray inside the autoclave, positioned so that the sample is near the rear of the chamber, and the door is closed.

- After approximately 45 minutes, the agent vapor concentration inside the headspace of the autoclave is monitored using a near-real time monitor (MINICAMS).

- Since the autoclave is limited to a maximum exposure time of 99 minutes for a single cycle, the autoclave is operated at 275 °F for two, 90-minute exposure cycles using the "Unwrapped" program cycle.

- A 10 to 12 minute period of time elapses between the two exposure cycles to permit recovery of the water and vapor condensate discharges collected from the first cycle.

- At the conclusion of the second 90-minute exposure cycle, the agent vapor concentration inside the headspace of the autoclave is monitored using a near-real time monitor (MINICAMS).

- The spiked sample is recovered from the autoclave and assayed for residual agent content along with the liquid and vapor condensate discharges from both exposure cycles utilizing the analytical protocols referenced in the Test Plan.

- The CycleStor data files detailing the operating conditions for each of the two cycles are downloaded for documentation.

- Following a test, with the autoclave empty, the autoclave is operated for a 90-minute exposure cycle at 275 °F followed by a 30-minute drying cycle to purge any residual VX from the autoclave chamber headspace and the discharge lines prior to the next test. This purge cycle typically occurs at the end of the day and the autoclave door remains latched in the closed position, but unsealed, overnight. Headspace monitoring of the autoclave chamber prior to a test yields VX concentrations at baseline levels (typically 0.02 to 0.06 VSL).

2.2 Waste Discharges

Again, the Test Plan presents a detailed description of the procedures employed to collect the waste discharges from the autoclave for subsequent agent analyses. To reiterate, there are two waste discharges from the autoclave:

- Water – In the "Unwrapped" cycle, 400 mLs of deionized water is automatically added into the autoclave chamber during the pre-vacuum stage. The loading inside the chamber is very small (10 grams of waste) compared to the 12-pound maximum loading limit for the "Unwrapped" cycle (according to the manufacturer's Operation Manual). Thus, only a small percentage of this water volume can be adsorbed into the waste matrix (this water is recovered from the waste matrix during the drying stage). Consequently, at the end of the exposure cycle, approximately 250 mLs of water remains inside the chamber. This excess water is expelled from the chamber by the pressure (~ 31 to 32 psig) present inside the chamber.

- Vapor Condensate – During the pre-vacuum and drying stages, the autoclave vacuum pump is used to attain a negative pressure (~ -10 to -13 psig) inside the chamber. As the vapor is pulled from the chamber it passes through a heat exchanger upstream of the pump. The discharge from the vacuum pump consists of condensate and vapors.

The original plumbing of the autoclave directed both of the waste discharges into a polymeric waste tank. Since the intent was to analyze each waste discharge separately, the plumbing was modified to accomplish this task. Figure 1 presents a schematic of the waste discharge collection system. The water discharge is routed to two, 500-mL traps in series immersed in ice. The vapor condensate discharge is routed to an identical 500-mL trap, followed by a 500-mL impinger filled with 150 mL of triacetin; again both vessels are immersed in ice. Please note that Figure 1 does not show the plumbing configuration that enabled the MINICAMS to directly monitor the headspace of the autoclave chamber. As discussed in the next section, this approach for the headspace monitoring had to be abandoned, and the plumbing was removed at the end of the initial test series. Hence, Figure 1 illustrates the system, as it existed for the 'official' performance tests.

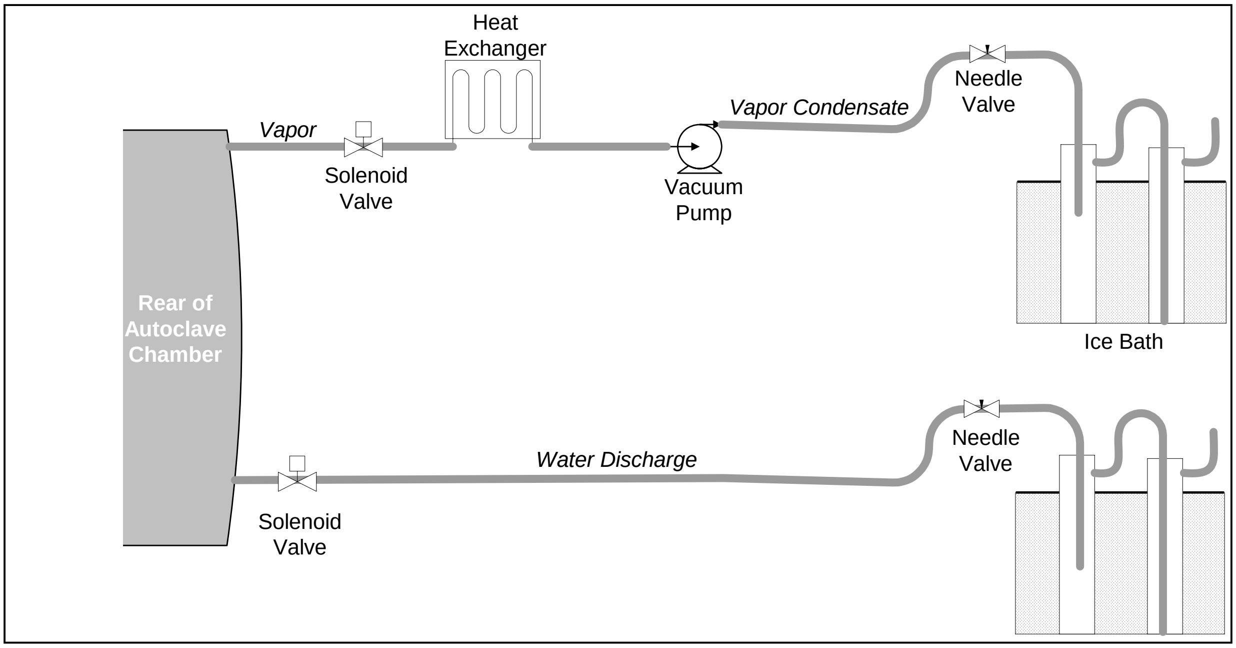

Figure 1. Waste discharge collection system.

3. FINDINGS

3.1 Initial VX Tests

A series of six (6) tests with VX agent were performed during which 'lessons learned' were discovered concerning the autoclave performance and the VX vapor monitoring technique. Subsequent modifications to the Test Plan were adopted to alleviate the discovered deficiencies. These initial tests are described below solely to document the rationale for the Test Plan modifications. The results for the remaining tests, as presented in the next section, represent the 'official' performance results obtained by the autoclave using the operating procedures as summarized above.

It is stressed that during the first five tests, the pre- and post-exposure vapor monitoring technique for the autoclave chamber headspace was implemented exactly as described in the Test Plan. That is, the chamber headspace was monitored directly by the MINICAMS using a port located in the rear of the chamber (see Figure 2). A series of two, 3-way valves were utilized to a vacuum pump to pull the chamber headspace sample into the MINICAMS during the pre- and post-exposure monitoring periods. During the autoclave cycle, the valves were switched to route the vapor discharge to the heat exchanger while the MINICAMS monitored the air inside the glove box.

For the pre-exposure monitoring, the autoclave door remained sealed (i.e., the chamber remained completely closed from the time the spiked sample was loaded into chamber until the monitoring began).

For the post-exposure monitoring, the automatic program sequence for the autoclave unseals the door at the conclusion of the drying period. However, the door remains latched in the closed position, and the MINCAMS pulled the headspace sample from the rear of the chamber.

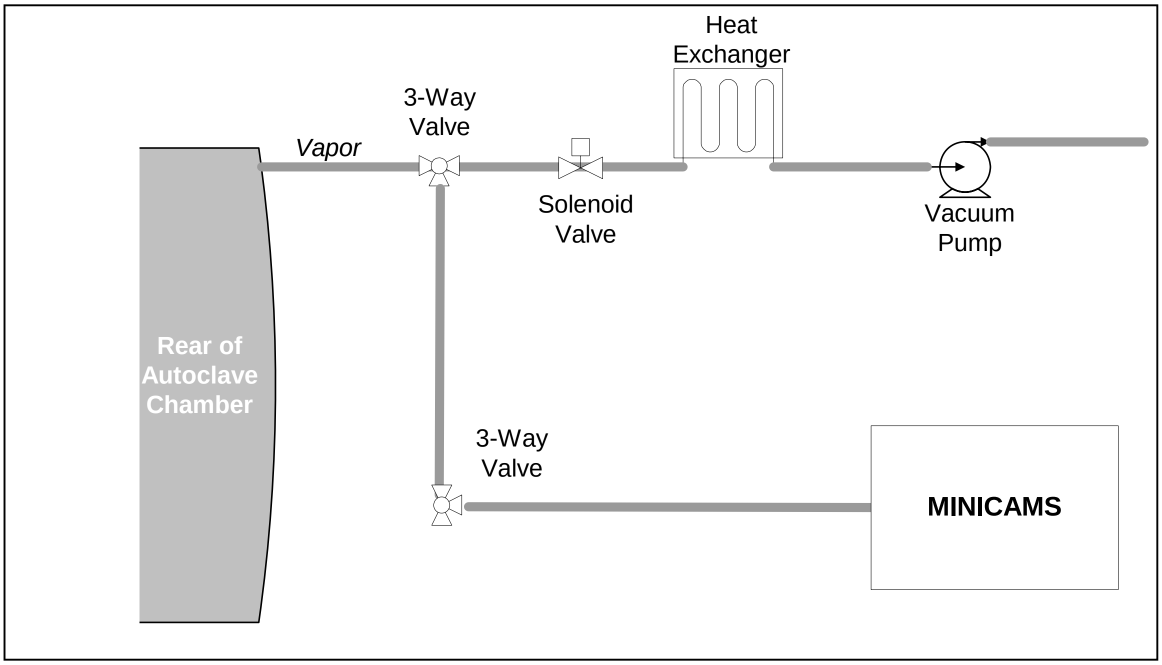

Figure 2. Direct headspace monitoring of autoclave chamber using MINICAMS.

3.1.1 VX – DPE Test #1

Preliminary tests performed by SwRI spiking onto wood with VX had indicated that a loading of approximately 400 µg of neat agent should yield a desirable vapor concentration within the 20-Liter chamber headspace (targeting a concentration of ~ 10 VSL). However, using this dosage mass in the first test with a 10-gram swatch of DPE (20-mil) only yielded a pre-exposure VX vapor concentration of 5.0 VSL. The autoclave cycle for this test was performed as detailed in the Test Plan: an "Unwrapped" cycle with a 60-minute exposure period at 275 °F followed by a 30-minute drying period. Following the conclusion of the drying period, the post-exposure VX vapor concentration inside the headspace was 0.48 VSL. Although the post-exposure vapor concentration was acceptable (i.e., < 1.0 VSL), the lower-than-anticipated vapor concentration obtained prior to initiation of the autoclave cycle caused us to seek a higher spiking level for the subsequent tests.

3.1.2 VX – DPE Tests #2 & #3

In these two tests, the autoclave operating conditions remained unchanged, but the spike level was increased to 900 µg of neat VX. Despite the increase, the pre-exposure VX headspace concentrations remained low (0.76 and 3.3 VSL for tests #2 and #3, respectively). The post-exposure vapor concentrations (0.32 and 0.57 VSL for tests #2 and #3, respectively) continued to show that the 60-minute exposure period and 30-minute drying period was yielding satisfactory results. The decision was made to keep the dosage at 900 µg for the upcoming tests of VX on wood.

3.1.3 VX – Wood Tests #1 & #2

Short segments of wooden dowels (untreated, 3/8-inch diameter) totaling 10 grams were used for the wood tests. A shallow depression was punched into the side of one of the dowel segments as a 'receptacle' for the VX spike. The spike loading remained at 900 µg and the autoclave operating conditions remained unchanged from the DPE tests. The pre-exposure VX vapor concentrations inside the chamber were comparable to the levels seen in the DPE tests (3.0 and 1.2 VSL for tests #1 and #2, respectively).

The post-exposure VX vapor concentration in Test #1 was 0.46 VSL, however, numerous interferences were observed in the MINICAMS chromatogram that may have affected measurement of the true agent concentration. Following the test, the heat-trace sampling line for the MINICAMS was cleaned and droplets of water were observed near the AgF conversion pad. The AgF conversion pad was replaced and additional heat tape was wrapped around the vapor sampling line at the rear of the autoclave chamber.

The post-exposure VX vapor concentration in Test #2 was 3.49 VSL, however, the validity of this measurement was uncertain, as the interferences were even worse than observed in the previous test despite the additional heat tape and line cleaning. Further investigation of the sampling line revealed that the AgF conversion was soaked by condensed water. Flushing the sampling line with solvent revealed traces of residue. It was apparent that moisture from the autoclave chamber was capable of entering the MINICAMS sample line, and that this moisture was gradually fouling the line and the AgF pad over successive cycles.

Therefore, to obtain reliable vapor concentration measurements, the monitoring approach given in the Test Plan (and illustrated in Figure 2) had to be abandoned. The pre- and post-exposure vapor monitoring of the chamber headspace is currently accomplished by inserting the MINICAMS sample line directly into the chamber via the door. A short length of ¼-inch stainless steel tubing is placed on the end of the MINICAMS heat-trace line, with an AgF conversion pad positioned on the distal end of the steel tubing. The length of the steel tubing is just long enough to place the AgF conversion pad in the middle of the autoclave chamber. To obtain the pre-and post-exposure vapor concentrations, the autoclave door is cracked open just wide enough to slip the ¼-inch stainless steel tubing past the door, and then the door is pressed tightly against the tubing.

3.1.4 VX – DPE Test #4

With the change to the vapor monitoring protocol, an additional test was performed using spiked DPE. The purpose of the test was to ascertain whether the changed protocol affected the promising results that were observed during the first three tests. This test did show that the vapor readings obtained by the MINICAMS utilizing the sampling line connected into the earlier tests were misleading:

- Spiking 900 µg of VX onto the DPE sample yielded a pre-exposure VX vapor concentration in the chamber headspace of 12.5 VSL, more than double the level seen in any of the prior measurements.

- After the completion of the 60-minute exposure period and 30-minute drying period, the post-exposure VX vapor concentration inside the chamber was 13.2 VSL. A second measurement collected 35 minutes later yielded a VX vapor concentration of 3.0 VSL.

- The autoclave cycle was repeated (60-minute exposure period and 30-minute drying period) on this same sample. The post-exposure VX vapor concentration inside the chamber following the second cycle was initially 3.3 VSL, with a second reading of 1.30 VSL obtained 14 minutes later.

The conclusions derived from these early tests were:

- The plumbing arrangement devised to enable the MINICAMS to directly sample the autoclave chamber obviously caused erroneously low VX vapor concentration measurements at both the pre- and the post-exposure time periods.

- Although cracking the door slightly ajar to insert the sample line into the autoclave chamber is less than ideal, it afforded more reliable vapor concentration measurements than the protocol originally specified in the Test Plan.

- The time required to achieve acceptable VX vapor concentrations (<1.0 VSL) inside the chamber was greater than could be achieved by a single cycle (limited by the autoclave program to 99 minutes). The decision was made to operate two consecutive cycles, each comprised of a 90-minute exposure period and a 30-minute drying period, for each test.

- The water and vapor condensate discharges for each of the two cycles in a test are collected at the completion of their respective cycle and analyzed separately (Tables 3 and 6).

3.2 Triplicate VX Test Results for DPE

Table 1 presents the headspace vapor measurements obtained for the ‘official’ triplicate autoclave tests performed with 900 µg of neat VX agent spiked onto 10-gram swatches of 20-mil DPE. To re-iterate, each test consists of two consecutive cycles, each comprised of a 90-minute exposure period and a 30-minute drying period. The post-exposure vapor concentration is obtained immediately after the completion of the drying period in the second cycle. In addition, a second post-exposure vapor concentration measurement is collected 28 minutes after the initial measurement (the MINICAMS sample/purge cycle for VX is 7 minutes; collecting a sample after 4 cycles was a somewhat arbitrary selection, but it approximated a 30-minute ‘hold’ period at the conclusion of a cycle that possibly might be imposed upon an operational autoclave before the door was opened).

Table 1. VX Vapor Headspace Concentrations inside Autoclave Chamber for DPE Spiked with 900 Micrograms of VX

Test	Pre-Exposure Concentration, VSL	Initial Post-Exposure Concentration, VSL	Post-Exposure + 28 Minutes Concentration, VSL
1	11.0	1.49	0.68
2	15.9	1.01	0.31
3	16.9	0.44	< 0.06

Table 2 summarizes: (1) the residual VX agent found in the spiked DPE sample after undergoing the two successive autoclave cycles in a test, and (2) the DRE percentage calculated by comparing the residual VX mass to the spike mass of 900 µg.

Table 2. VX DRE for DPE Spiked with 900 Micrograms of VX

Test	Residual VX in DPE, micrograms	DRE, percent
1	0.055	99.994
2	0.100	99.989
3	0.249	99.972

Table 3 summarizes: (1) the volumes of water and vapor condensate collected at the conclusion of the two individual autoclave cycles in each test, (2) the concentration of VX agent found in the water and vapor condensate samples, and (3) the total mass of VX agent in the water and vapor condensate samples.

Table 3. VX in Discharges for DPE Spiked with 900 Micrograms of VX

Test	Cycle	Discharge	Volume, mL	VX concentration, nanograms/mL	Mass of VX, micrograms
1	1	Water	265	6.94	1.84
		Condensate	160	22.3	3.57
	2	Water	290	2.43	0.71
		Condensate	155	3.44	0.53
2	1	Water	265	7.48	1.98
		Condensate	160	21.2	3.40
	2	Water	270	3.22	0.87
		Condensate	155	3.81	0.59
3	1	Water	260	8.25	2.15
		Condensate	155	26.0	4.03
	2	Water	280	3.69	1.03
		Condensate	160	5.91	0.94

A discussion of these results will follow the presentation of the VX and wood test results.

3.3 Triplicate VX Test Results for Wood

Table 4 presents the headspace vapor measurements obtained for the ‘official’ triplicate autoclave tests performed with 900 µg of neat VX agent spiked onto 10-grams of wooden dowel segments. To re-iterate, each test consists of two consecutive cycles, each comprised of a 90-minute exposure period and a 30-minute drying period. The post-exposure vapor concentration is obtained immediately after the completion of the drying period in the second cycle. In addition, a second post-exposure vapor concentration measurement is collected 28 minutes after the initial measurement.

Table 4. VX Vapor Headspace Concentrations inside Autoclave Chamber for Wood Spiked with 900 Micrograms of VX

Test	Pre-Exposure Concentration, VSL	Initial Post-Exposure Concentration, VSL	Post-Exposure + 28 Minutes Concentration, VSL
1	39.3	0.63	0.16
2	37.0	0.73	< 0.06
3	46.6	0.55	0.07

Table 5 summarizes: (1) the residual VX agent found in the spiked DPE sample after undergoing the two successive autoclave cycles in a test, and (2) the DRE percentage calculated by comparing the residual VX mass to the spike mass of 900 µg.

Table 5. VX DRE for Wood Spiked with 900 Micrograms of VX

Test	Residual VX in Wood, micrograms	DRE, percent
1	6.42	99.29
2	1.21	99.87
3	4.58	99.49

Table 6 summarizes: (1) the volumes of water and vapor condensate collected at the conclusion of the two individual autoclave cycles in each test, (2) the concentration of VX agent found in the water and vapor condensate samples, and (3) the total mass of VX agent in the water and vapor condensate samples.

3.4 EA2192 Tests

During the DPE and wood tests, SwRI was tasked to evaluate whether the VX degradation product EA2192 was present either in the autoclaved waste matrix or in the waste discharges. To detect and quantify EA2192, SwRI utilized a high performance liquid chromatography/mass spectrometry (HPLC-MS) analytical procedure previously developed to quantify agent decomposition products (ADPs) for the JACADS closure. Since this procedure requires extraction of solid matrices using HPLC-grade water, the EA2192 analysis could not be accomplished on the same waste sample analyzed for residual VX (i.e., the latter requires extraction with IPA/DCM solvent). Thus, separate autoclave tests had to be performed for the EA2192 analyses.

Table 6. VX in Discharges for Wood Spiked with 900 Micrograms of VX

Test	Cycle	Discharge	Volume, mL	VX concentration, nanograms/mL	Mass of VX, micrograms
1	1	Water	270	6.05	1.63
		Condensate	157	12.5	1.97
	2	Water	280	5.26	1.47
		Condensate	160	2.93	0.47
2	1	Water	262	9.50	2.49
		Condensate	158	11.2	1.77
	2	Water	250	6.88	1.72
		Condensate	162	3.05	0.49
3	1	Water	260	8.15	2.12
		Condensate	155	16.5	2.56
	2	Water	280	6.68	1.87
		Condensate	160	3.97	0.64

Two tests were performed for the EA2192 evaluations – one with DPE and one with wood dowels. The autoclave operational parameters were identical to the prior VX tests (two consecutive cycles, each comprised of a 90-minute exposure period and a 30-minute drying period) and the VX spiking mass remained unchanged (900 micrograms). The EA2192 results are presented in Table 7. No detectable concentrations of EA2192 were measured in any of the spiked waste samples or in the discharges.

Table 7. EA2192 Results for DPE & Wood Spiked with 900 Micrograms of VX

Sample I.D.	Volume, mL	EA2192 ppb (ng/mL)	EA2192, micrograms
10-grams DPE spiked w/900 ug VX	-	< 2	< 0.10
DPE, Water Cycle 1	260	< 2	< 0.52
DPE, Water Cycle 2	259	< 2	< 0.52
DPE, Condensate Cycle 1	165	< 2	< 0.33
DPE, Condensate Cycle 2	160	< 2	< 0.32
10-grams wood spiked w/900 ug VX	-	< 2	< 0.10
Wood, Water Cycle 1	260	< 2	< 0.52
Wood, Water Cycle 2	275	< 2	< 0.55
Wood, Condensate Cycle 1	162	< 2	< 0.32
Wood, Condensate Cycle 2	159	< 2	< 0.32

4. DISCUSSION

Some general observations concerning the tests:

- The collection traps, immersed in ice, used to collect the water and vapor condensate discharges yielded remarkably comparable volumes among the 12-autoclave cycles that comprised the triplicate series of DPE and wood tests.

    - Two traps in series are used to collect the water discharge from the chamber that occurs at the conclusion of the exposure period. Despite being a single discharge event under pressure (~ 31 to 32 psig) and at temperature (275 ºF), all but 5 to 10 mLs of the water is collected in the first trap. The installation of a needle valve to limit the flow rate of the water discharge from the autoclave chamber is largely responsible for the efficient collection by the first trap.

    - In contrast to the water discharge, the vapor condensate discharge consists of a slow, trickle that occurs intermittently during the pre-vacuum and the drying stages. It was apparent that the heat exchanger on the autoclave efficiently condenses the water vapor to enable effective collection by the discharge trap.

- The operational data collected by the CycleStor data system showed, for the DPE and wood tests, that the autoclave operated in a fairly repeatable manner. Chamber temperatures during the exposure stages were typically in the range of 276 to 277 ºF at pressures of 31 to 32 psig. Subsequent to these tests, a lag thermometer was inserted into the chamber to confirm chamber temperatures. This calibrated instrument showed that the actual chamber temperature was nominally a couple of degrees higher than indicated by the CycleStor data.

Regarding the analytical results for the tests:

- The average post-exposure VX vapor headspace concentration immediately following the conclusion of the drying stage for the triplicate DPE tests was close to the 1.0 VSL target (0.98 VSL average). Within 28 minutes, the VX vapor concentration inside the chamber was comfortably below the 1.0 VSL criteria.

- In the wood tests, the post-exposure VX vapor headspace concentration immediately following the conclusion of the drying stage was below the 1.0 VSL limit in all 3 tests.

- The DRE for the DPE tests exceeded 99.9 percent, while the wood tests yielded a DRE of greater than 99.0 percent.

- The VX agent trends for the water and condensate discharges differed between the two test substrates.

    - In the DPE tests:

        - The cumulative mass of VX found in the two discharges during the first cycle was consistently greater (by a factor of at least 3) than the total mass collected from both discharges in the second cycle. This would indicate that most of the VX emissions occurred during the first cycle, which is a reasonable expectation.

    - Furthermore, in the first cycle of the DPE tests, the mass of VX in the condensate was approximately double the mass detected in the water discharge.

    - In the second cycle of the DPE tests, the masses of VX in the condensate and water discharges were very similar to one another.

- In the wood tests, however:

    - While the mass of VX discharged during the first cycle was greater than the second cycle, the difference was not as significant as seen in the DPE tests. This would indicate that the VX release during the second cycle was still prominent and probably the impetus for a lower DRE compared to DPE.

    - There was little disparity between the masses of VX detected in the condensate compared to that observed in the water discharges during the first cycle of the wood tests.

    - Finally, while the mass of VX in the condensate dropped significantly during the second cycle of the woods tests, there was only a small decrease in the mass of VX found in the water discharged in the second cycle compared to the first cycle.

5. CONCLUSION

The initial tests yielded information regarding the length of the exposure cycles to achieve VX vapor headspace concentrations near the 1.0 VSL targeted criteria. These tests also showed that some modification to the originally envisioned headspace monitoring approach was needed to obtain reliable VX vapor concentrations.

Once the cycle lengths and headspace monitoring methodology were refined, the subsequent experiments yielded insight into the performance results associated with autoclaving wood and DPE contaminated with neat VX agent under the defined test conditions. The extrapolation of these results to a full-scale, operational system is beyond the scope of this 'proof-of-concept' experimental program.

One cautionary note is made regarding the interpretation of the residual VX mass present in the 10-gram waste samples following the two consecutive autoclave cycles (Tables 2 and 5). Using the 10-gram weight of the spiked sample to calculate a residual VX concentration (e.g., ppb of VX in the 'treated' waste) could be misconstrued or deceptive regarding the autoclave performance capability. The 900 micrograms of neat VX occupied a minute portion of the surface area represented by the 10-gram sample. If the waste samples had been even larger (i.e., up to the maximum load limit of 12 pounds for this autoclave model), the identical spike loading likely would have yielded about the same residual mass of VX after treatment, but it would equate to a much lower VX residual on a concentration (ppb) basis.